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UNITED STATES PATENT APPLICATION

OF

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FOR

METHOD FOR PRODUCING TEXTURED THERMOPLASTIC FILM

This application claims rights of priority from U.S. Provisional Patent Application Serial No. 60/065,699, filed on November 14, 1997, which is hereby incorporated by reference.

BACKGROUND OF THE INVENTION

This invention relates to a method for producing coated and uncoated thermoplastic articles and, more particularly, relates to improved methods for providing smooth upper and lower surfaces to a thermoplastic substrates that are particularly useful in optical media applications, such as CD-ROM cards. Such applications require the use of substrates having polished surfaces on both sides and a birefringence of less than twenty-five (25) nm. Further requirements for optical media applications include abrasion, chemical and UV radiation resistance, and clarity. Moreover, thermoplastic films must transmit, rather than reflect, light to be acceptable for optical applications.

Polycarbonate films generally have acceptable levels of clarity, and strength, but lack acceptable levels of birefringence, abrasion resistance, chemical and UV radiation resistance, and smoothness for optical applications. For example, uncoated polycarbonate films generally have high birefringence, which is in part due to the levels of stress which are placed on the film during its formation. This stress is frozen into the film upon cooling. Moreover, uncoated polycarbonte films generally have poor abrasion resistance and chemical resistance. Uncoated polycarbonte films are also susceptible to degradation by UV radiation.

Radiation curable acrylic coatings and methods for their application to polycarbonate substrates are known. (See, e.g., European Patent No. 228,671). While conventional methods exist for applying radiation curable acrylic coatings to polycarbonate film, the adhesion of these cured coatings to the underlying polycarbonate can be less than desirable. Moreover, conventional methods do not carefully control the smoothness of the films, which is critical for optical applications. For these reasons, polycarbonate films have not been compatible with optical applications because the required adhesion, clarity and smoothness properties have not generally been attainable prior to the present invention.

Conventional radiation curable acrylic coating compositions are also problematic because they employ non-reactive solvents to reduce the viscosity of the coating compositions during application thereof to the polycarbonate substrate. These non-reactive volatile components must later be eliminated from the coatings by applying a forced hot air drying system, which may produce a coating having unacceptable bubbles and surface roughness. It is also undesirable to use coating compositions containing substantial levels of non-reactive, volatile components such as solvents, because they create environmental and safety concerns.

Abrasion resistant thermoplastic films having improved optical properties may be manufactured by curing a solvent-free radiation curable coating composition after application to the surface of a polymeric sheet or film. This curing process may be accomplished by directing radiant energy through the substrate opposite the surface being coated. This "cold-casting technique" is further illustrated in U.S. Patent No. 5,468,542, to Crouch, which is hereby incorporated by reference. Although improved surface characteristics can be achieved with the radiation curable coating compositions disclosed in U.S. Patent No. 5,468,542, such coated thermoplastic films are not suitable for optical applications because no effort

is made to match the indices of refraction of the coating and substrate to avoid light reflection at the interface (i.e., provide a low delta refractive index).

In summary, conventional methods are inadequate for producing thermoplastic film suitable for use in optical media applications, because such methods do not produce thermoplastic film that has acceptable levels of birefringence, abrasion resistance, chemical and UV resistance, smoothness, and clarity together with a low delta refractive index (i.e., the difference in refractive index between the coating and the substrate). Specifically, birefringence, which is related to the residual stress in the film upon molding and cooling, must preferably be kept below 25 nm. Also, the film must be polished on both sides to avoid light scattering. Moreover, if the film is coated, the delta refractive index must be sufficiently low to avoid unacceptable light reflection at the interface.

It is also generally known in theory to produce polycarbonate films by extruding heated resin and passing the extruded resin through a nip between two polished metal rolls. This process is unsuitable for producing low birefringence films because it introduces a high level of stress in the films which increases the birefringence of said films.

In view of the foregoing, it would be advantageous to provide thermoplastic films which are suitable for optical media applications. It would further be desirable to provide an efficient method for making such films which avoids the shortcomings of the prior art.

Accordingly, it is one object of the invention to provide coated thermoplastic films wherein the top and bottom surfaces are sufficiently smooth to avoid unacceptable light scattering, and the Delta refractive index between the coating and film is sufficiently low to avoid unacceptable light reflection at the interface.

It is another object of this invention to provide a method for producing coated and uncoated thermoplastic films, which method does not require

using solvents or other volatiles which may lead to imperfections in the films and present environmental concerns.

It is another object of this invention to provide a method of making coated films which exhibit good adhesion between the coating and the film substrate.

It is yet another object of the invention to provide a method of making a coated film having low birefringence.

It is another object of the invention to provide a method of making a one-side textured, one-side polished film substrate having low residual stress that may be coated to form a film having two smooth surfaces.

It is a further object of the invention to provide a method of making a coated thermoplastic film which is compatible with optical applications wherein the coating adheres strongly to the substrate.

SUMMARY OF THE INVENTION

The method according to the present invention for producing coated thermoplastic articles suitable for optical applications comprises a first step of passing a substrate thermoplastic film through a pair of rollers wherein the top roller is covered with a smooth, low friction material which textures the upper surface of the substrate, and the bottom roller is metallic and polishes the lower surface of the substrate. This first step of the process produces a substrate having a textured top side and a polished bottom side. The low friction top roller preferably has sufficiently low friction such that the top side of the film has an opportunity to "slip" such that stress is reduced in the film below what would be obtained if the top roller were also metallic. This reduction in stress produces a substrate having lower birefringence.

Next, a curable coating is applied to the upper surface of the substrate, and is cured. Upon curing, the curable coating forms a smooth coating upon the upper surface of the substrate. This coating is sufficiently smooth to avoid unacceptable scattering of a light beam impinging upon said surface. The

curable coating composition is preferably selected such that the substrate and the coating have a sufficiently low delta refractive index to avoid unacceptable reflection of light at the interface between the coating and the substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a horizontal elevational schematic view of equipment involving a casting drum for practicing the method of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention involves a method to produce a coated thermoplastic film suitable for optical application exhibiting exceptional smoothness of both upper and lower surfaces and low birefringence. The method includes first producing a low stress, one-side textured, and one-side polished polycarbonate film, wherein the textured side eighty-five degree (85°) gloss, measured in accordance with ASTM D523, which is incorporated by reference herein, is in the range of 90% to 100%. The Ra (surface roughness) of the uncoated substrate film is twenty (20) to forty (40) nm, and is preferably produced by using super smooth polytetrafluoroethylene (hereinafter "PTFE") TEFLON® material, having a surface roughness (hereinafter "Ra") of 0.3 to 0.8 μm, as the covering on the top roll. The bottom roll, which produces the polished side of the film, uses a standard chrome plated steel roll. The textured side of the film substrate is smoothed with a curable coating to an Ra of three (3) to ten (10) nm. This idea can be applied to other amorphous and crystalline thermoplastic materials, and is not limited to polycarbonate. Optical media applications generally require a film that has a polished surface on both sides and a birefringence of less than twenty-five (25) nm. Other requirements include abrasion and ultraviolet (UV) resistance, substrate thickness consistency and ability to die cut the cured article immediately after lamination. Another requirement is that the substrate

should be a barrier to water vapor. For purposes of this invention, a lower delta refractive index produces better results. Specifically, the delta RI is preferably less than 0.08, and more preferably is less than 0.05. A coating formulation disclosed in co-pending Application Serial No. 09/034,883, which is hereby incorporated by reference, meets these criteria.

The present invention discloses a novel process technique that will produce a low stress polycarbonate film (0.005" to 0.030") that retains an excellent surface appearance. This technique can produce film with birefringence of less than twenty-five (25) nm and a surface gloss of ninety-two percent (92%). The substrates used in this process are preferably made from a polycarbonate resin. A preferred polycarbonate substrate for the method of the present invention is one formed from a thermoplastic polycarbonate material, such as LEXAN® resin, a product of General Electric Company. Typical examples of polycarbonate resins are described in U.S. Pat. No. 4,351,920, which is incorporated herein by reference, and are obtained by the reaction of aromatic dihydroxy compounds with phosgene. Other polycarbonate resins may be obtained by the reaction of aromatic dihydroxy compounds with carbonate precursors such as diaryl carbonates. U.S. Pat. No. 4,351,920 also describes various methods for the preparation of aromatic polycarbonate resins, which may be used as substrates in the present invention. A preferred aromatic dihydroxy compound is 2,2-bis(4-hydroxy phenyl) propane, (i.e., Bisphenol-A). The term aromatic polycarbonate resins is also meant to include polyester carbonates obtained from the reaction products of a dihydroxy phenol, a carbonate precursor and a dicarboxylic acid such as terephthalic acid and isophthalic acid. Optionally an amount of a glycol may also be used as a reactant. Polycarbonate film may be made by well-known methods. Typically, the molten thermoplastic is cast onto an extrusion roll stack, and both sides of the material are polished and pressed to a uniform thickness. Preferably the polycarbonate film has a thickness of

from five (5) to twenty (20) mils.

The ultraviolet radiation-curable coating compositions are generally comprised of monomers and oligomers containing acrylic, methacrylic, and vinylic unsaturation as well as other 100% solids convertible materials (e.g., monomer-soluble polymers and elastomers, inorganic silica fillers and pigments and the like, etc.). The coating systems generally comprise monomers having molecular weights of from about 100 to 1000, and having single unsaturation or di-, tri-, or higher multi-functional unsaturation sites. In the practice of the present invention, the coating is preferably substantially free (of less than one percent (1%)) of volatile, non-reactive components. The coating compositions are preferably ninety-nine percent (99%) to 100 percent by weight reactive components and solid materials. In a more preferred version, the coatings are 99.9 percent to 100 percent by weight reactive components and solid materials. In a most preferred version, the coatings are 100 percent by weight reactive components and solid materials. The solid materials may include non-volatile solid materials such as polymeric materials and colloidal silica. Suitable polymeric materials include cellulose acetate butyrate. The coating composition is preferably 100 percent convertible to solids upon exposure to ultraviolet radiation. The composition also contain an amount of a photoinitiator effective to permit photo curing of the composition. In a preferred embodiment, the curable coating composition comprises approximately 98 wt% of an acrylate, and 2 wt% of a photoinitiator.

The preferred acrylic coating composition contains a substantial level of a relatively low molecular weight aliphatic alkane diol diacrylate which will penetrate, via diffusion, the region below the surface of polycarbonate substrate upon contact and exposure to elevated temperatures. A suitable aliphatic alkane diol diacrylate is 1, 6-hexanediol diacrylate. A preferred acrylate coating composition contains from five percent (5%) to sixty percent

(60%) by weight of an aliphatic alkane diol diacrylate based on the total weight of the coating composition. The aliphatic diol diacrylate preferably contains from two (2) to twelve (12) carbon atoms in the aliphatic portion thereof. Suitable aliphatic diol diacrylates include ethylene glycol diacrylate, butane diol diacrylate, hexane diol diacrylate, octaine diol diacrylate, decane diol diacrylate. A preferred coating composition contains about thirty-seven percent (37%) by weight trimethylolpropane triacrylate (TMPTA), about fifteen percent (15%) by weight dipentaerythritol monohydroxy pentacrylate (DIPEPA) thirty-seven percent (37%) by weight 2, 6-hexanediol diacrylate, about nine percent (9%) cellulose acetate butyrae (CAB) and about two percent (2%) by weight of the photoinitiator, diethoxyacetophenone (DEAP). A preferred silica filled acrylic coating employs a mixture of twenty-two percent (22%) 1, 6-hexanediol diacrylate, twenty-two percent (22%) trimethylolpropane triacrylate, thirty-five percent (35%) functionalized colloidal silica, seven percent (7%) of a latent ultraviolet radiation absorber such as benzene sulfonate ester of Cyasorb Registered TM 5411 (BSEX) as described by D.R. Olson, J. Applied Polymer Science 28, 1983, p. 1159, incorporated herein by reference and three percent (3%) of a photoinitiator such as diethoxyacetophenone (DEAP). Suitable functionalized colloidal silica is set forth in Olson et al., U.S. Patent No. 4,455,205; Olson et al., U.S. Patent No. 4,491,508; Chung, U.S. Patent No. 4,478,876, and Chung, U.S. Patent No. 4,486,504, all incorporated herein by reference.

Abrasion resistant thermoplastic composites having improved optical properties may also be made by effecting the cure of a solvent-less radiation curable coating composition which has been applied onto the surface of a polymeric sheet or film. The cure of the applied coating material can be effected while it is in contact with a smooth surface (cold casting) by directing radiant energy through the substrate opposite the surface being coated. (See, e.g., U.S. Patent No. 5,455,105, which is hereby incorporated by reference)

The "cold-casting technique" is further illustrated in U.S. Patent No. 5,468,542, issued to Crouch, which is incorporated by reference herein.

Accordingly, the low stress film is produced by:

(Step 1) Producing a one-side textured, and one-side polished polycarbonate film. The textured side eighty-five degree (85°) gloss is in the range of ninety percent (90%) to 100%. The Ra (surface roughness) of the uncoated film is twenty (20) to forty (40) nm and is produced by using super smooth PTFE material (Ra of 0.3 to 0.8 μm) as the covering on the top roll. The bottom roll uses a standard chrome polish material, wherein Ra =0.05 μm.

(Step 2) Smoothing the textured side in step 1 with a curable coating to an Ra of three (3) to ten (10) nm.

Examples

The following examples are provided merely to show one skilled in the art how to apply the principles discussed herein. These examples shall not be used to limit the scope of the appended claims.

Example 1: A coating suitable for application to a one side polished, one side textured film.

The present example shows that best balance of optical, chemical, and abrasion resistance is given by the following coating formulation: 1 percent (1 %) Irgacure 819 photoinitiator, (phenyl bis (2,4,6 trimethyl benzoyl), 1 percent Darocur 1173 photoinitiator, ten percent (10 %) FCS100, and eighty-eight percent (88 %) RX-0726. The coating surface must be as smooth as possible to prevent laser scattering. Since the reflected laser signal contains the audio and video information from the CD-ROM, if scattering occurs, the information will be lost. It has been determined through experimentation that the coating finish must have a maximum Rz value of 2.0 microns or less.

Formulation	Diameter Laser	Diffraction Spots	Finish (Rz)	Comment

Control	0.7 mm	none	Laser only, no sample
1	0.45	yes	10 micron
2	0.60	no	2 micron
3	0.50	yes	6 micron
4	0.50	yes	5 micron

The tested formulations were as follows: Formulation #1 is = 88 wt% RX0726, 10% FCS100, and 2% Lucirin TPO; Formulation #2 is = 88 wt% RX0726, 10% FCS100, and 1% Darocur 1173, and 1% Irgacure 819; Formulation #3 = 88 wt% RX0726, 10% FCS100, and 2% Darocur 1173; and Formulation #4 is 88 wt% RX0726, 10% FCS100, 1% Lucirin TPO, and 1% Darocur 1173.

From the table above, it is apparent that formulation #2, which incorporates an organic compound, a photoinitiator and a silicone coating solution exhibits improved surface smoothness, and consequently, less laser scattering. While Lucirin TPO and Darocur 1173 provide adequate cross-linking in the bulk, only the combination of Darocur 1173 and Irgacure 819 provide adequate cross-linking in the bulk and surface. If the surface is not completely cross-linked, the finish will be compromised. It will be immediately recognized by those skilled in the art, however, that variations on the above Examples may provide equally improved results and are all within the intended scope of the present invention.

Example 2: A process for coating a one-side polished, one-side textured film.

A suitable apparatus for applying and curing a coating on the surface of a polymeric substrate in accordance with the method of the present invention is depicted in FIG. 1. In FIG. 1, radiation-curable coating material 10 is continuously applied by flowing it onto the surface of the film at a controlled rate.

Substrate roll 12 is formed from a roll of uncoated substrate 14 surrounding a core 16. Substrate 14 is unwound pursuant to the movement of casting drum 18 (described below). Coating material 10 is applied to the surface of substrate 14 by dripping it onto the substrate 14 using an applicator 20. It will be apparent to those skilled in the art that adjustments may be made in the coating system in order to apply the coating to the substrate efficiently. Coating material 10 may be applied to substrate 14 by any of a number of well-known roll coating methods, such as spraying, brushing, curtain coating, and dipping, as well as other well-known roll coating methods, such as reverse roll coating, etc. The thickness of radiation-curable coating 10 applied to the substrate and the thickness of the resultant cured hard coat 21 is dependent upon the end use of the article and the physical properties desired, and their thickness may range from about 0.05 mil to about 5.0 mils for the nonvolatile coating. The preferred thickness is from about 0.2 mil to about 1.0 mil.

After coating material 10 is applied to substrate 14, the Coated substrate 22 is guided to nip roll 24. The choice of materials which form the nip roll 24 used in the present invention is not critical. The rolls may be made of plastic, metal (i.e. stainless steel, aluminum), rubber, ceramic materials, and the like. Nip roll 24 may be provided with a sleeve, preferably formed from a resilient material such as PTFE or polypropylene, or from one of the variety of currently available synthetic rubber compounds and blends thereof. The sleeve is snugly fitted over the roll surface to provide a smooth, friction-minimizing surface for contacting substrate 22. Nip roll 24 is adjustable relative to the position of casting drum 18, described below, and may optionally be independently driven.

As shown in FIG. 1, casting drum 18 is situated in a position adjacent nip roll 24, such that the outer circumferences of nip roll 24 and drum 18 are

adjacent to each other at an interface defining a nip 26 which is described below. The applied pressure at the interface of nip roll 24 and drum 18 may be adjusted by well known methods, such as air cylinders (not shown), attached to the axle 28 of nip roll 24, which selectively urges the roll toward drum 18. Typically, the applied pressure at the interface is slight, i.e. less than five (5) pounds per linear inch, when the substrate is not passing through nip 26. The applied pressure can be readjusted according to a variety of parameters when a substrate having a coating thereon is passing through nip 26, as described below.

Casting drum 18 surrounds central axle 19, and is preferably made from a material which is conductive to heat, and preferably comprised of stainless steel or chromium-plated steel. Furthermore, it is preferred that the drum be independently driven by an outside power source (not shown).

Casting drum surface 30 may be provided with a wide variety of textures or patterns, depending upon the texture or pattern desired to be imparted to coating 10 and the resultant hardcoat 21. For instance, surface 30 may be provide with a highly polished chrome-plated surface if a high degree of gloss is desired for the hardcoat 21. If a lower sheen is desired for the hardcoat 21, surface 30 may be less polished so as to provide a matte texture to the coating. Similarly, a design pattern may be embossed on surface 30 to impart a mirror-image design pattern to hardcoat 21. The cured coating will create a hardcoat 21 which will thus become a permanent mirror-image of casting drum surface 30.

Although a nitrogen blanket may be employed to ensure an anaerobic cure of the coating composition it is preferred that an anaerobic cure be obtained without the use of such a nitrogen blanket. In order to minimize the presence of air in the coating 10 prior to curing, without the use of a nitrogen gas blanket, the pressure capable of being exerted at nip 26 is carefully adjusted. The adjustment of applied pressure at nip 26 may be accomplished

as described above. To obtain a certain coating thickness the exact pressure that will be exerted at nip 26 will depend on factors such as the viscosity of coating 10, the substrate speed, the degree of detail in the design pattern on surface 30 (if present), and temperature of the casting drum. Typically, for a substrate having a thickness of fifteen (10) mils having applied thereon an acrylic-based coating having a thickness of 0.8 mil and a viscosity of 400 centipoises, at a substrate speed of fifty (30) feet per minute and a roll cover of 30 durometer hardness (Shore A) a nip pressure of twenty-five (25) pounds/linear inch is applied to the coated substrate. Coating 10 is thereby pressed into contact with both substrate 22 and casting drum surface 30, thereby ensuring that there is a substantial absence of free diatomic oxygen from the coating during curing, so as the ensure a substantially complete curing of the coating and a cured coating, hardcoat 21, exhibiting a mirror image of the texture and/or pattern of casting drum surface 30. Excess coating forms a bead 31 of uncured coating composition material above the nip and across the width of the drum. This bead 31 ensures that adequate coating material enters through the nip 26 across the width of the drum.

After substrate 22 having coating 10 applied thereon passes through nip 26, the coating may be cured by means of ultraviolet radiant energy. As shown in FIG. I, means 32 transmits ultraviolet radiation energy into a surface 34 of substrate 22 opposite a surface 36 having coating 10 thereon. The radiant energy passes through the transparent substrate 22 and is absorbed by the coating 10, the latter being compressed between substrate 22 and drum surface 30. The preferred wavelength of the UV radiation is from about 2900 Angstroms to about 4050 Angstroms. The lamp system used to generate such UV radiation may consist of discharge lamps, e.g. xenon, metallic halide, metallic arc, or high, medium, or low pressure mercury vapor discharge lamps, etc., each having operating pressures of from as low as a few millitorrs up to about ten (10) atmospheres. The radiation dose level applied to coating

10 through substrate 22 may range from about two (2.0) J/cm^2 to about ten (10.0) J/cm^2. A typical curing system suitable for the present invention is a Linde medium pressure mercury lamp, as described in U.S. Pat. No. 4,477,529. The number of lamps directing light to the surface of the substrate is not critical; however, a greater number of lamps may allow a higher production rate for the substrate having coating 10 thereon. Typically, two lamps, each producing 300 watts/linear inch of radiant energy, are sufficient for an acrylic-based coating having a thickness of about 0.5 mil, when the production line speed is approximately fifty (50) feet/minute. Such a curing procedure should result in both the polymerization of the polyfunctional acrylic monomers and the cross-linking of the polymers to form hard, non-tacky coatings. The coating may receive the post curing by further exposure to ultraviolet radiation after leaving the surfaces of the casting drum.

After the layer of coating material has been applied to and cured on substrate 22 according to the method of the present invention, the resulting product is a hard coated polycarbonate film article 38 which is guided around idler rolls 40, 42 and 44 then collected on take-up roll 46, the latter typically being independently driven and capable of separating the hard coated polycarbonate article 38 from drum surface 30.

Example 3: Forming a low birefringence one-side polished, one-side textured substrate film.

The one sided textured polycarbonate film (0.005" to 0.030") is made by extrusion. The melt is forced into a nip between two (2) rolls. The gap between the rolls determines the film thickness. The thickness consistency is +/- five percent (5%) for a 0.010"film. This film is produced using a super smooth, insulating, PTFE sleeved roll with Ra surface roughness of twenty (20) to forty (40) nm on the top surface. The bottom roll is highly polished

chrome. A more complete description of this apparatus appears in co-pending Application Serial No. 09/034,883, which is hereby incorporated by reference.

The coating is applied to the textured side of the substrated film to smooth out the surface. During the curing of the coating, the heat tends to further anneal the film and reduce the stress level. The gloss is measured at 60° with the backside painted black. The coating also provides improved abrasion, and chemical resistance and provides a barrier to water vapor (WVTR). Taber Abrasion Resistance (ASTM D1044) for a CS10F wheel, 500 grams, and 100 cycles in a change in percent (%) haze of between five to thirty (5-30). Chemical resistance (determined via a 24 hour surface exposure test at 120°F.) is exhibited for these common household materials (coffee, Chlorox, ketchup, and tea). The measured WVTR for an acrylic coated 0.010" polycarbonate film was 0.5 to 1.0 grams water/100 in^2/24 hours. This WVTR measurement was performed at 73°F, and 100% relative humidity with a wet filter material, which was covered by glass to maintain control conditions. Furthermore, said film was placed under water and in similar conditions as above for one (1) week, and evidenced no failure nor damage. A suitable PTFE finishing roll sleeve for extruded plastic film in an optical media application is disclosed in co-pending application Serial. No. 09/044,890.